

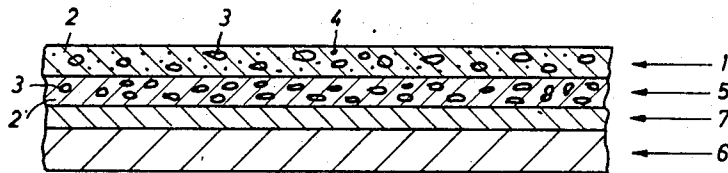
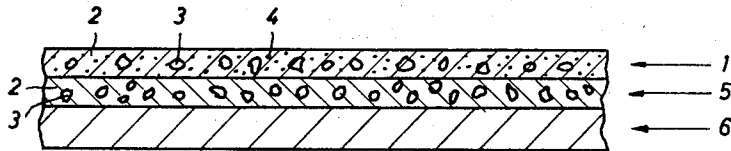
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3,679,410

HEAT-SENSITIVE RECORDING MATERIAL

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3,679,410

HEAT-SENSITIVE RECORDING MATERIAL

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Continuation-in-part of application Ser. No. 608,571, Jan. 11, 1967. This application Nov. 23, 1970, Ser. No. 91,864

Claims priority, application Great Britain, Jan. 11, 1966, 1,350/66

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48 Claims

ABSTRACT OF THE DISCLOSURE

A heat-sensitive recording material containing a thermosensitive recording layer comprising hydrophobic thermoplastic particles dispersed in a hydrophilic binder and in underlying contacting relation to said recording layer an underlayer having a hydrophilicity and removability with water less than that of said recording layer and which contains at least one thermoplastic substance having a hydrophobic character and a melting or softening point such that said substance remains adherent after heating to the heat coalesced hydrophobic thermoplastic particles contained in the hydrophilic binder of the recording layer.

According to a preferred embodiment the interlayer has been prepared from a latex containing polymer particles which coalesce on drying the coated layer at room temperature. The interlayer may contain hydrophilic pigments such as colloidal silica and a hydrophilic binder that is preferably less soluble in water than the hydrophilic binder of the recording layer and the weight ratio of polymer particles relative to the hydrophilic binder is preferably at least 1:1.

The present invention relates to the recording and reproduction of information and to recording materials for use in a recording method, based on information-wise heating of a heat-sensitive recording element.

The present application is a continuation-in-part of the patent application No. 608,571, now abandoned, filed Jan. 11, 1967.

In the Belgian patent specification 656,713 a recording material is described which contains a heat-sensitive layer comprising thermoplastic polymer particles dispersed in a hydrophilic binder.

In the U.S. Pat. 3,476,937 a recording layer is described comprising a hydrophilic binder incorporating hydrophobic thermoplastic particles in heat-conductive relationship with at least one light-absorbing substance wherein absorbed light is transformed into heat. Heat produced in such substance and conducted to the thermoplastic particles produces in the recording layer a decrease in water-permeability and water-solubility.

According to an embodiment described in said U.S. patent specification for recording and producing a copy of an original, the image-wise differentiation in water-solubility is utilized for removing the recording layer in the non-heated or insufficiently heated areas e.g. by washing away or degrading the hydrophilic binder. Thus, when the recording layer comprises a pigment or dissolved dye-stuff a copy of the original is formed by applying the washing away technique.

Dependent on the properties of the support for the recording layer an opaque or transparent copy of the original is produced.

The present invention is concerned with improvements in heat-sensitive recording materials which are capable of

being used to record information in terms of a difference in the water-permeabilities of different areas of the recording layer, and is in particular concerned with recording processes wherein after the information-wise heating of the recording material the still water-permeable or relatively more water-permeable areas of the recording layer are removed by means of water or an aqueous liquid. The various refinements or developments above referred to, for instance, permitting a heat pattern to be generated internally of the recording material by irradiating this material, are compatible with the present invention and may be adopted in the performance thereof.

In order to obtain sharp copies of the original on applying the washing-away technique, a recording material is needed the recording layer of which strongly adheres to its base in the heated areas. Indeed, for selectively washing away the non-heated or insufficiently heated portions of the recording layer in a small lapse of time, it may be required to rub the recording layer, e.g. with a sponge-like element soaked with water. If the heated portions of the recording layer do not adhere appreciably more strongly to the base material than the non-heated portions, the rubbing of the recording layer in wet state or the tearing out of swollen non-heated portions may result in a damaging of the image or in a loss in image sharpness.

It has now been found that the wet removal of the non-heated portions of a heat-sensitive recording material can be effected more selectively when in the heat-recording process a heat-sensitive recording material is used comprising a heat-sensitive recording layer containing hydrophobic thermoplastic particles dispersed in a hydrophilic binder and which layer is in contacting relationship with an underlayer containing one or more thermoplastic substances having a hydrophobic character and a melting or softening point such that said substances remain adherent to the coalesced hydrophobic thermoplastic particles contained in the hydrophilic binder of the recording layer when melted or softened by the information-wise heating of the heat-sensitive recording material and wherein said interlayer is characterized by a lesser water-permeability and removability with water than said recording layer.

It is preferred for the said interlayer to comprise hydrophobic thermoplastic substances having a softening or melting point equal to or lower than that of the hydrophobic thermoplastic polymer particles in the recording layer. The use of thermoplastic substances with a melting or softening temperature which is higher is not excluded, however, since in that case only a higher imaging temperature has to be applied.

During the exposure of a heat-sensitive recording material according to the invention, the hydrophobic thermoplastic polymer particles must be heated in such a degree that they coalesce in the exposed areas of the recording layer, and in order that the coalesced polymer particles will strongly adhere to the thermoplastic substance in the underlying layer, this substance has to be softened or melted by the same heat. The thermoplastic substance, moreover, must be sufficiently hydrophobic to bind or to adhere to the hydrophobic thermoplastic polymer in the recording layer. If the interlayer is too hydrophobic, difficulties will be encountered in obtaining a good adhesion to it of the recording layer. A certain content of wetting agent and/or hydrophilic binder can be incorporated into the interlayer to provide a good anchorage. An improved anchorage can also be obtained by electrostatically charging the interlayer and/or support before applying the composition for forming the recording layer.

According to a first embodiment the interlayer on which the recording layer is formed comprises a dispersion of

thermoplastic polymer particles (i.e. a latex) in a continuous phase, e.g., a hydrophilic binder. The interlayer acting as a subbing layer contains preferably hydrophobic thermoplastic polymer particles in a hydrophilic binding agent that is less soluble in water than the hydrophilic binding agent of the recording layer. For instance, the interlayer contains gelatin hardened to some degree with e.g. formaldehyde and the recording layer contains polyvinylalcohol. The binding agent for the hydrophobic polymer particles contained in the interlayer may be water-insoluble but is preferably less hydrophobic than said particles. A suitable binding agent is a copolymer of mainly hydrophobic vinyl monomers e.g. styrene, butadiene and vinylidene chloride and a minor amount of hydrophilic monomer or monomers e.g. methacrylic acid, itaconic acid and n-tert.butylacrylamide.

According to a second embodiment the interlayer is a thermoplastic polymer layer e.g. prepared from a latex containing hydrophilic pigment particles e.g. colloidal silica, optionally together with a hydrophilic binding agent. For instance the interlayer contains hydrophobic thermoplastic polymer particles dispersed in a binder which may be a latex (a so-called "soft" latex) the polymer particles of which coalesce and form a continuous phase on drying the coated layer at room temperature (20° C.) together with hydrophilic pigment particles e.g. zinc oxide, silica and titanium dioxide. A latex dispersion contains any necessary wetting agent for keeping the polymer particles dispersed in aqueous or hydrophilic medium.

According to a third embodiment the interlayer essentially consists of coalesced hydrophobic thermoplastic polymer particles. For example the interlayer is a polyethylene layer applied from a polyethylene latex of which the polyethylene particles have been coalesced by heating above their melting temperature.

According to a modification of that embodiment the interlayer is prepared from a soft latex (i.e. a latex the polymer particles of which have a melting or softening point below room temperature) that on drying at room temperature forms a layer of coalesced hydrophobic polymer particles.

The interlayer when containing a hydrophilic binding agent contains it in a ratio by weight with respect to the hydrophobic material preferably smaller than the ratio by weight of the hydrophilic binding agent to hydrophobic thermoplastic particles contained in the recording layer.

The hydrophobic substances of the recording layer and interlayer have preferably the same chemical structure but may have a different chemical structure provided they wet (i.e. adhere to) each other in fused or softened state, as is the case e.g. with polystyrene and polyethylene polymer particles.

In preferred combinations the hydrophobic substances of said layers are compatible (i.e. miscible) in fused state. As preferred hydrophobic substances thermoplastic polymer particles applied from a latex are used but layers applied from aqueous wax particle dispersions as e.g. described in the U.S. patent specification 3,156,183 are not excluded.

The U.S. patent specification 3,476,937 and the published Dutch patent application 66/6,719 contain data relating to heat-sensitive recording layers which are applicable in carrying out the present invention and these documents should therefore be read in conjunction herewith.

By the image-wise applied heat, the interlayer is more firmly bound to the recording layer in the heated areas than in the non-heated areas. This can be explained in terms of a so-called fusion-junction in said heated areas between said interlayer or self-supporting sheet and the recording layer. In other words the coalesced hydrophobic polymer particles of the recording layer remain after the information-wise heating adherent to the hydrophobic substance of the interlayer in corresponding with the information-wise heated areas. The interlayer may be applied

directly to a support, in respect of which it possesses a proper adhesive power, or may be applied to a support which is precoated with one or more intermediate subbing layers in order to obtain at storage temperature a sufficient adhesion between said interlayer and the support.

Having stated in general the concepts of this invention a detailed description will now be made of the composition and structure of preferred heat-sensitive materials according to the invention and their use in heat-recording processes.

FIGS. 1 and 2 of the accompanying drawing are enlarged sectional views of representative types of heat-sensitive materials according to the present invention.

As illustrated in FIG. 1 a particular heat-sensitive material according to the present invention contains:

A heat-sensitive recording layer 1 comprising a hydrophilic binder 2, dispersed hydrophobic thermoplastic polymer particles 3, and dispersed substances 4, which absorb copying light and transform said light into heat;

An interlayer (i.e. subbing layer) 5 comprising a hydrophilic binder and dispersed thermoplastic polymer particles having a melting or softening point which is lower than, equal to or not substantially higher than that of the particles 3 present in the recording layer;

A support 6 which may be an opaque or transparent support, e.g. a cellulose triacetate support or polyethylene terephthalate support.

As illustrated in FIG. 2 a heat-sensitive material according to the present invention contains:

A heat-sensitive recording layer 1 as described for FIG. 1;

An interlayer (subbing layer) 5 having the same composition as described for FIG. 1;

A subbing layer 7 for a support 6;

A support 6, e.g. a cellulose triacetate or polyester support.

Suitable subbing layers capable of adhering hydrophilic layers such as gelatin-containing layers to cellulose triacetate and polyethylene terephthalate supports are well known from the silver halide photographic art.

The hydrophilic binder of the recording layer and occasionally that of the interlayer may, e.g., constitute a hydrophilic natural colloid, a modified hydrophilic natural colloid, or a synthetic hydrophilic polymer or polycondensation product. More particularly said binding agent may be selected from natural or modified natural hydrophilic colloids, e.g. gelatin, glue, casein, zein, hydroxyethylcellulose, carboxymethylcellulose, methylcellulose, carboxymethyl hydroxyethylcellulose, gum arabic, sodium alginate and hydrophilic derivatives of such colloids. They may also be selected from synthetic hydrophilic polymers such as, e.g., polyvinyl alcohol, poly-N-vinylpyrrolidone, polyvinylamine, polyethylene oxide polymers, polystyrene sulphonic acid, polyacrylic acid and hydrophilic derivatives of such polymers.

The hydrophilic binder material for use in the recording layer of the heat-sensitive recording materials according to the present invention is preferably water-soluble at room temperature (20–25° C.). In this respect poly-N-vinylpyrrolidone, polyvinyl alcohol, polyethylene oxide and gelatin containing a softening agent, e.g. urea, are preferred.

When the interlayer contains a hydrophilic binder it does not necessarily mean that the interlayer in the non-exposed areas becomes washed away together with the portions of the recording layer. It will remain by using a hydrophilic binder which is not soluble enough in water during the washing step. As is well known an increase in water-resistance of a hydrophilic binder or colloid can be obtained by hardening. A suitable hardenable hydrophilic colloid is, e.g., gelatin. Several methods for hardening gelatin are generally known. A very useful combination of binders is gelatin and poly-N-vinyl-pyrrolidone, the former being used in an interlayer and the latter in the

recording layer. The poly-N-vinylpyrrolidone is more water-soluble than gelatin at room temperature.

So, according to a preferred embodiment of the invention a completely transparent interlayer is used, which contains dispersed hydrophobic thermoplastic particles in a hydrophilic binder, which is less water-soluble than the hydrophilic binder of the recording layer.

Information about the kind and preparation of thermoplastic hydrophobic polymer particles suitable for use in the heat-sensitive recording layer as well as in the interlayer can be found, e.g. in the U.S. patent specification 3,476,937.

The recording layer contains preferably at least 50% by weight of the dispersion consisting of the hydrophilic binder and the hydrophobic thermoplastic polymer particles dispersed therein, and should be coated and dried in such conditions that it is water-permeable at a temperature, e.g., not substantially higher than room temperature. The polymer particles being solid at room temperature preferably soften between 10 and 200° C. above room temperature. It is preferred to use in the recording layer and in the underlying interlayer polymers having a melting point or glass-transition temperature between 10 and 200° C. above room temperature.

More particularly are suitable, e.g. polyethylene and polyvinylidene chloride having a melting point of 110 and 190° C. respectively, and the following polymers with their respective glass-transition temperatures: polystyrene (100° C.), polymethyl methacrylate (comprised between 70 and 105° C.), polyethyl methacrylate (50° C.), polyvinyl chloride (near 70° C.), polyacrylonitrile (near 100° C.), poly-N-vinylcarbazole (200° C.).

The polymer selected for the interlayer has preferably a melting point or glass-transition temperature below that of the polymer in the recording layer or not substantially higher, e.g. has a melting point in the range of 20° C. above and 20° C. below the melting point of the coalescible polymer particles in the recording layer.

As is known, the glass-transition temperature can be lowered by the addition of some substances called plasticizers. More particulars about suitable plasticizers and the glass-transition temperature of homo- and copolymers can be found e.g., in Georges Champetier, *Chimie Macromoléculaire—Généralités*, Librairie Armand Colin—Paris Veme, pp. 194–198. It appears therefrom that a range of glass-transition temperatures can be obtained, a given glass transition temperature being determined by the ratio of the monomers of condensation reagents used during the copolymerisation or copolycondensation. Thermoplastic hydrophobic polymers covering a wide range of molecular weights may be used in materials according to the present invention both in the recording layer and in the interlayer. Polymers possessing a molecular weight ranging from 5000 to 1,000,000 are preferred.

Polyethylene possessing a molecular weight of 15,000 to 50,000 was found to be very suitable. Of course, mixed dispersions of polymer particles may also be used and in the case of the recording layer different polymer particles may occasionally contain reaction components, which at the moment of diffusing into one another as a result of the application of heat or pressure react with one another, e.g., with resulting formation of colour.

Preferred hydrophobic thermoplastic homopolymers and copolymers suitable for the manufacture of a recording layer and/or interlayer according to the present invention are applied as an aqueous dispersion containing a hydrophilic binding agent. The aqueous dispersion of the homopolymer or copolymer is prepared preferably by radical polymerisation in emulsion of one or more polymerisable monomers according to known techniques, e.g., those described by W. Sörenson and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, Interscience Publishers, New York (1961). In the radical polymerisation use is made of dispersing agents such as those described by K. Laux, "Die Grenzflächenaktiven Stoffe"

in Winnacker-Küchler's "Chemische Technologie," Carl Hanser Verlag, Munich (1960), pp. 155–242.

Aqueous dispersions of polymers prepared by dispersing a solution of a water-insoluble polymer in a water-immiscible volatile solvent in an aqueous solution of a hydrophilic binding agent are also considered. As solvents may be mentioned, e.g., chlorinated hydrocarbons such as methylene chloride and trichloroethylene.

Further, polymer dispersions, which are appropriate for use in the recording layer and/or interlayer of a material according to the present invention can be obtained by mechanically dispersing in water finely divided polymer particles, preferably with the help of surfactants and/or hydrophilic protective colloids such as polyvinyl alcohol and gelatin. Latices obtained by emulsion polymerisation are preferred. In this polymerisation technique one or more monomers are dispersed by stirring them to very fine droplets in the presence of water, emulsifiers such as soaps, ammonium oleate, sulphonated fatty alcohols and the like, protective colloids such as carboxymethylcellulose, polyvinylalcohol and the like, a buffering system, a surfactant and a water-soluble catalyst, e.g., hydrogen peroxide or a persulphate. The polymer is obtained as a stable dispersion of polymer particles in water.

The size of the polymer particles in dispersion may vary from 0.01 μ to 50 μ . However, in connection with the recording layer it is noted that the larger the particles the less is the resolving power. Very good results are obtained with dispersions the dispersed polymer particle size of which varies from 0.05 μ to 20 μ . Dispersions wherein the size of the dispersed particles varies from 1 μ to 1m μ are considered as colloidal systems. A colloidal system the continuous phase of which is formed by water (dispersing medium) and the dispersed phase of which is formed by particles having a size varying from 1 to 0.001 μ is called a hydrosol. Good results are obtained when using hydrosols the polymer particles of which are not greater than 0.1 μ .

The ratio by weight of thermoplastic polymer particles to hydrophilic binder in the recording layer as well as in the interlayer (if the latter contains a hydrophilic binder) is preferably greater than 1:1, more preferably greater than 3:2. For instance when using gelatin as the binding agent in the interlayer the ratio by weight of gelatin to polymer particles is 1 to 3 and when using polyvinylalcohol 1 to 6. The amount by weight of thermoplastic polymer particles comprised in the recording layer and an interlayer containing such particles is preferably in the range of 0.5 g. to 10 g./sq. m.

Recording layers and interlayers used in the present invention preferably each have a thickness from 0.5 μ to 10 μ .

According to a preferred embodiment, the recording layer of the recording material contains, colored substances e.g. pigments or dyes preferably in water-insoluble state. These substances may absorb copying light and transform said light into heat. Preferred substances absorbing visible light and infrared light and converting said light into heat are dark coloured or black pigments, e.g., finely divided carbon black, graphite, prussian blue, oxides, sulphides or carbonates of heavy metals, particularly of those heavy metals having an atomic weight between 45 and 210, such as manganese or lead sulphide or these heavy metals themselves in finely divided state such as silver, bismuth, lead, iron, cobalt, and nickel.

According to a particular embodiment the heat-sensitive material can be made sensitive to light of a limited region of the visible spectrum. This can be done by incorporating into the heat-sensitive layer coloured substances, which absorb light of a part of the visible spectrum and convert that light into heat as described in the published Dutch patent application 6606719. A thermographic layer spectrally sensitized in that way can be used for recording coloured originals in terms of differences in water-solubility and wash-off removability.

It is to be understood that mixtures of said coloured substances can be used too, so that light of the whole visible spectrum is absorbed. The said substances need not necessarily absorb in the range of the visible spectrum alone, they may also absorb to some extent infrared light, which light is normally produced to some extent by flash lamps.

Coloured substances or mixtures of said substances when used for optical sensitization of the thermographic recording layer preferably absorb light corresponding to at least one of the primary additive colours (red, green, blue) or subtractive colours (cyan, magenta, yellow). Substances that absorb light of a part of the visible spectrum and wherein absorbed light energy is transformed into heat are, e.g., dyes belonging to the classes of the azo dyes, the triarylmethane dyes, the xanthene dyes, the acridine dyes, the methine dyes, the azine dyes, the phthalocyanine dyes, the anthraquinone dyes and allied dyes. Said dyes can be used and dispersed as well as in dissolved form. The substances absorbing light and converting it into heat are preferably present in the recording layer in a concentration providing an optical density of at least 1 when direct exposure is applied, and in a concentration providing an optical density of 0.25 to 0.80 when the recording material is used in a reflectographic exposure technique. When in dispersed form, the copying light absorbing substances have preferably a particle size not greater than 0.1μ .

The information-wise heating of the recording material may proceed according to various ways.

According to a common heat-recording process the heat accumulated in the image areas of an original by infra-red irradiation is used to produce the necessary image differentiation in the heat-recording layer. In that heating process the recording layer does not contain pigments or dyes that are infra-red absorbing or when pigments or dyes are present they absorb that radiation only to a minor extent.

Another procedure which has proved to give very good results, is to use a type of recording material according to the present invention, wherein the recording layer contains a substance that absorbs copying light (i.e. infrared light and visible light, or visible light alone) and converts that light into heat, and to image-wise irradiate this recording material. This irradiation produces an internal image-wise heating resulting in the desired differentiation in water-absorption power and water-solubility of the recording layer.

In the above embodiment transmission exposure or contact-exposure as well as reflex exposure can be applied. When applying a reflex copying method, the intensity of exposure, the concentration of substances absorbing copying light and the thermoplastic polymer particles present in the recording layer are chosen in such a way, that the heating resulting from the absorption of the light rays directed to the original and striking undifferentially the heat-sensitive layer causes at most (practically no or) only a slight loss of water-permeability and/or water-solubility in the heat-sensitive recording layer. In other words, the image-wise heat resulting from the image-wise reflected light must produce in the recording layer a practically useful level of differentiation in swelling power or solubility in water.

According to a particular embodiment, an image of heat-absorbing material is produced in the interlayer or recording layer by means of light-sensitive silver halide contained in both or one of said layers. The said silver halide is image-wise exposed and developed. The silver image obtained acts as heat-absorbing image for producing by an overall exposure to light, e.g. infra-red light, the desired useful differentiation of swellability or solubility in water.

For reflex exposure the support and different layers of the recording material should obviously be sufficiently

transparent. When applying a transmission or contact printing process, however, the recording layer or any layer or support of the recording material may be opaque as well as transparent. In order to prevent lateral diffusion of heat and loss of image sharpness the exposure time preferably does not exceed 10^{-1} sec.

Suitable radiation sources producing copying light of high intensity in a very small lapse of time and which are very suitable for application with recording materials containing light-absorbing substances converting that light into heat are the so-called flash lamps. Good results are obtained with xenon gas discharge lamps, which can supply a light energy of 100 to 1000 watt.sec. in a time interval of 10^{-5} to 10^{-2} seconds. These flash-lamps emit a greater part of energy as visible light than as infrared light. Details about a copying apparatus containing such a discharge lamp can be found in Belgian patent specification No. 664,868.

Evidently gas discharge lamps with a lower energy output can be used if the emitted energy is focused onto a relatively small heat-sensitive area. So, e.g., a gas discharge lamp with an energy output of 40 watt.sec. is suited for copying 6 cm. x 6 cm. x 9 cm. originals on heat-sensitive materials as described in the present invention. For materials having an optical density of at least 1 resulting from the presence in the recording layer of light-absorbing substances, a light-energy of at least 0.1 watt.sec. per sq. cm. will be required for the desired image differentiation. In practice an exposure of 0.3 watt.sec. per sq. cm. will provide satisfactory results. It is further self-explanatory that exposure may be progressive and intermittent. In other words the original may be scanned, e.g., by a high-intensity light spot rapidly line-wise scanning the original, or may be progressively exposed through a laterally moving slit wherein, e.g., copying light of a tube-like radiation source is focused.

It is evident that the heat-sensitive recording material, before or during the creation of the image-wise heat differentiation, can be subjected to overall heating to a certain temperature below the temperature at which a substantial decrease in swelling or solubility in water takes place.

After producing the image-wise differentiation in water-permeability and wash-off removability of the recording layer the exposed material is processed by washing away the unexposed areas or by swelling the unexposed portions and removing them by tearing out with simultaneous transfer to a receiving material, e.g., a porous paper sheet.

The following examples illustrate the present invention.

EXAMPLE 1

A poly(ethylene terephthalate) support of 0.1 mm. thickness provided with a subbing layer for gelatin is coated with the following composition pro rata of 30 g. per sq. m.:

	G.
10% aqueous gelatin solution	400
40% aqueous dispersion of polyethylene having a particle size of less than 0.1μ and an average molecular weight comprised between 15,000 and 30,000, melting point 110° C.	320
Water	240
10% aqueous saponine	40
3% aqueous solution of the sodium salt of the condensation product of oleic acid and methyltaurine	40
4% aqueous formaldehyde	20

The interlayer thus obtained is dried at 30° C.

On this layer a heat-sensitive layer, for use in a washing-away development by rubbing with a cotton pad soaked

with water of 20° C., is coated pro rata of 30 g. per sq. m. from the following composition:

	G.
10% aqueous solution of polyvinyl alcohol -----	45
40% aqueous dispersion of polyethylene as described above -----	60
Water -----	320
Aqueous carbon dispersion containing per 100 g. 53 g. of carbon (average particle size 0.1 μ), 23 g. of water, 18 g. of glycol and 6 g. of nonylphenyl polyethylene oxide -----	8
3% aqueous solution of the sodium salt of tetradecyl sulphate -----	25

After drying, the material is contact-exposed through a negative transparency being a reproduction of a printed text. The exposure is carried out by means of a xenon gas discharge lamp placed at a distance of 4 cm. of the recording layer and having a capacity of 1000 watt.sec., producing light in a time of $\frac{1}{2000}$ sec.

After exposure the recording layer is rubbed with a cotton pad wetted with water of 20° C., in this way removing the non-exposed and still water-permeable parts of the recording layer.

EXAMPLE 2

A poly(ethylene terephthalate) support of 0.1 mm. thickness provided with a subbing layer for gelatin is coated with the following composition pro rata of 25 g./sq. m.:

	G.
40% aqueous dispersion of polyethylene (see Example 1) -----	80
Water -----	320

The interlayer thus obtained is dried at 130° C.

On this layer a heat-sensitive layer is coated pro rata of 30 g./sq. m. from the following composition:

	G.
Polyethylene glycol with a molecular weight of 6000 -----	20
40% aqueous dispersion of polyethylene (see Example 1) -----	80
Water -----	325
Aqueous carbon dispersion (see Example 1) -----	50
3% aqueous sodium tetradecyl sulphate -----	25

Exposure and development occur as described in the foregoing Example 1.

EXAMPLE 3

To a paper support coated with polyethylene and weighing 120 g./sq. m. an interlayer is applied from the following composition pro rata of 30 g./sq. m. and then dried at 30° C.

	G.
10% aqueous gelatin -----	200
40% aqueous dispersion of polyethylene (see Example 1) -----	160
Water -----	120
10% aqueous saponine -----	20
50% aqueous solution of the sodium salt of the condensation product of oleic acid and methyl taurine -----	20
4% aqueous formaldehyde -----	10
Polyethylene glycol with an average molecular weight of 20,000 -----	10

On this layer a heat-sensitive layer is coated pro rata of 30 g./sq. m. from the following composition:

	G.
20% aqueous solution of polyethylene glycol with an average molecular weight of 200,000 -----	200
40% aqueous dispersion of polyethylene (see Example 1) -----	80
Water -----	145
Aqueous carbon dispersion (see Example 1) -----	40
3% aqueous solution of sodium tetradecylsulphate --	25

Recording and development occur as described in Example 1.

EXAMPLE 4

5 A poly(ethylene terephthalate) support of 0.1 mm. thickness is coated with the following solution pro rata of 15 g./sq. m.:

	G.
40% aqueous dispersion of polyethylene as described in Example 1 -----	50
20% aqueous dispersion of polyethyl acrylate (soft latex) -----	50
30% aqueous dispersion of silica having a particle size of 25 mm. -----	50
15 Water -----	750
Ethanol -----	100

After drying at 60° C., the subbing layer obtained is coated with a heat-sensitive layer from the following composition in a proportion of 20 g./sq. m.:

	G.
10% aqueous solution of polyvinylpyrrolidone having an average molecular weight of 30,000 -----	170
40% aqueous dispersion of polyethylene as described in Example 1 -----	195
Aqueous carbon dispersion containing per 100 g.: 16 g. of carbon and 2 g. of low viscous poly(N-vinylpyrrolidone) -----	450
Water -----	120
30 3% aqueous solution of the sodium salt of tetradecyl sulphate -----	65

After drying at 50° C., the material obtained is exposed and developed as in Example 1.

EXAMPLE 5

To a poly(ethylene terephthalate) support of 0.1 mm. thickness the following composition is applied pro rata of 20 g./sq. m.:

	G.
40% aqueous dispersion of polyethylene described in Example 1 -----	50
20% aqueous dispersion of copoly(vinylidene chloride/N - butylmaleimide/itaconic acid) (83/15/2) -----	50
Water -----	750
30% aqueous dispersion of silica having a particle size of 25 mm. -----	50
50 Ethanol -----	100

After drying at 60° C., the subbing layer obtained is coated with a heat-sensitive layer as described in Example 4. After drying again, the material obtained is exposed and developed as in Example 1.

EXAMPLE 6

60 The same recording material as described in Example 5, after exposure as described in Example 1, is moistened with water by dipping it for 15 seconds in water of 20° C. and thereupon led between two pressure rollers while in contact with a gelatin subbing layer present on a transparent cellulose triacetate support. On emerging between the rollers the two materials are peeled apart. After the said separation the gelatin subbing layer bears a positive black image of the original, whereas on the polyethylene terephthalate support of the recording material a black negative image is left.

EXAMPLE 7

75 A poly(ethylene terephthalate) support of 0.1 mm. thickness provided with a subbing layer for gelatin is

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coated for forming an interlayer with the following composition pro rata of 30 g. per sq. m.:

	G.	
10% aqueous gelatin solution -----	300	
40% aqueous dispersion of polyethylene having a particle size of less than 0.1 μ and an average molecular weight comprised between 15,000 and 30,000 -----	375	
Water -----	240	
10% aqueous saponine -----	40	10
3% aqueous solution of the sodium salt of the condensation product of oleic acid and methyl-taurine -----	40	
4% aqueous formaldehyde -----	20	

The interlayer thus obtained is dried at 30° C.

On this layer a heat-sensitive layer, for use in a washing-away development by rubbing with a cotton pad soaked with water of 20° C., is coated pro rata of 30 g. per sq. m. from the following composition:

	G.	
10% aqueous solution of polyvinyl alcohol -----	60	
40% aqueous dispersion of polyethylene as described above -----	60	
Water -----	320	
Aqueous carbon dispersion containing per 100 g. 53 g. of carbon (average particle size 0.1 μ), 23 g. of water, 18 g. of glycol and 6 g. of nonylphenyl polyethylene oxide -----	8	25
3% aqueous solution of the sodium salt of tetradecyl sulphate -----	25	30

After drying, the material is contact-exposed through a negative transparency being a reproduction of a printed text. The exposure is carried out by means of a xenon gas discharge lamp placed at a distance of 4 cm. of the recording layer and having a capacity of 1000 watt.sec., producing light in a time of $\frac{1}{2000}$ sec.

After exposure the recording layer is rubbed with a cotton pad wetted with water of 20° C., in this way removing selectively the non-exposed and still water-permeable parts of the recording layer.

EXAMPLE 8

To a poly(ethylene terephthalate) support of 0.1 mm. thickness the following composition is applied pro rata of 20 g./sq. m.:

	G.	
30% aqueous dispersion of polystyrene (average particle size 0.13 μ and average molecular weight 50,000) -----	70	50
20% aqueous dispersion of copoly(vinylidene chloride/N - butylmaleimide/itaconic acid) (83/15/2) -----	50	
Water -----	750	
30% aqueous dispersion of silica having a particle size of 25 nm. -----	50	55
Ethanol -----	100	

After drying at 60° C., the subbing layer obtained is coated with a heat-sensitive layer as described in Example 4. After drying again, the material obtained is exposed and developed as in Example 1.

EXAMPLE 9

A poly(ethyleneterephthalate) support provided at both sides with a semi-transparent coating containing silica to give it the properties of a drafting film (prepared as described furtheron) was provided with a subbing layer of the following composition in a ratio of 15 g. per sq. m.:

Water -----	g--	746	70
Colloidal silica having an average particle size of 5 nm. -----	g--	17	
40% by weight aqueous dispersion of polyethylene having a particle size of less than 0.1 μ and an average molecular weight comprised between			75

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15,000 and 30,000, melting point 110° C.ml--	33
35% by weight aqueous dispersion of the copolymer of styrene, butadiene, acrylonitrile and methacrylic acid (45/33/7/15% by weight) -----ml--	4
30% by weight aqueous dispersion of colloidal silica of an average particle size of 0.025 nm.ml--	120
Ethanol -----ml--	80

The subbing layer thus obtained was dried at 50° C.

To the dried subbing layer a thermosensitive recording layer was applied in a ratio of 20 g. per sq.m. from the following composition:

Water -----ml--	212
20% by weight aqueous poly-N-vinylpyrrolidone solution (average molecular weight 30,000)ml--	75
20% by weight aqueous dispersion (latex) of polyethylene prepared as described hereinafterml--	190
Aqueous carbon dispersion containing per 100 g.: 16 g. of carbon black and 2 g. of low viscous poly-N-vinylpyrrolidone) -----ml--	330
30% by weight aqueous dispersion of silica (average particle size 0.025 nm.) -----ml--	75
Ethylene glycol -----g--	3
Ethanol -----ml--	115

After drying, the material was contact-exposed through a negative transparency being a reproduction of a printed text. The exposure was carried out by means of a xenon gas discharge lamp placed at a distance of 4 cm. of the recording layer and having a capacity of 1000 watt.sec., producing light in a time of $\frac{1}{2000}$ sec.

After exposure the recording layer was rubbed with a cotton pad wetted with water of 20° C., in this way removing the non-exposed and still water-permeable parts of the recording layer.

Preparation of polyethylene latex

In a 400 ml. metal pressure tube were placed:

Partly oxidized polyethylene prepared according to United Kingdom patent specification No. 997,135 filed Oct. 25, 1963 by W. R. Grace & Co., by the oxidation of polyethylene (average molecular weight: 7000, crystalline melting point: 125-130° C., acid number: 26-30) -----g--	40
n-Hexadecyloxy-decycloxyethylene -----g--	12.4
Water -----ml--	150

The pressure tube was sealed and rotated at 30-40 r.p.m. and heated at 190-200° C. for 1 hour in order to make a latex dispersion. Then the tube was allowed to cool slowly to room temperature. Yield: 200 ml. of a slightly beige latex of pH 9.

Preparation of the drafting film

35 g. of very pure crystalline silicon dioxide having an average particle size of 5 nm. and 3.5 g. of monobutylphosphate were dispersed for 4 hours in 140 ml. of 1,2-dichloroethane.

The following components were then added consecutively to the resulting dispersion:

43.5 g. of soluble partially cured melamineformaldehyde resin	
215 g. of a polyesteramide of adipic acid, ethylene glycol, and ethanolamine, which has been modified with p-toluene diisocyanate,	
3.5 g. of titanium dioxide with an average particle size of 0.1 nm. (matting agent), which had been dispersed previously with monobutyl phosphate in methyl ethyl ketone;	
4.35 g. of a 50% by weight solution of p-toluene sulphonic acid in methanol.	

The resulting mixture was stirred for 3 hours and filtered.

The mixture was then diluted with 1,2-dichloroethane to a concentration of approximately 20 g. of solids in 100

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ml. A ml. of methyl polysiloxane was added as levelling agent per 100 ml. of lacquer composition.

This lacquer composition was applied at both sides of a polyethylene terephthalate film support which was subbed at both sides with a layer of a copolymer of vinylidene chloride, N-tert.butylacrylamide, n-butylacrylate, and N-vinylpyrrolidone (ratios by weight: 70:23:3:4).

The lacquer composition was applied in such a way that, after drying at 100° C. the resulting layer had a thickness of approximately 5 μ .

The thus obtained drafting film was at one side coated with the subbing layer and thermosensitive layer as described above.

EXAMPLE 10

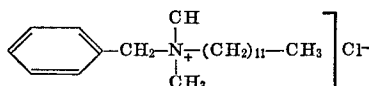
To a poly(ethylene terephthalate) support of 0.1 mm. thickness the following composition for forming a subbing layer was applied pro rata of 13 g. per sq. m.:

40% by weight aqueous dispersion of polyethylene having a particle size of less than 0.1 μ and an average molecular weight comprised between 15,000 and 30,000 -----	15
20% by weight aqueous dispersion of the copolymer of vinylidene chloride, n-tert. butylacrylamide and itaconic acid (88/10/2% by weight) -----	12
30% by weight aqueous dispersion of colloidal silica having an average particle size of 25 nm. -----	12
Water -----	811
Ethanol -----	150

After drying at 50° C. the obtained subbing layer was coated with the following composition for forming a thermosensitive layer:

Water -----	432
Pigment Red 146 (C.I. 11,000), an aqueous dispersion of a monazo pigment of a 3-hydroxy-2-naphthoic arylide sold under the trade name Permanent Carmin FBB Colanyl Teig by Farbwerke Hoechst AG Frankfurt (M), Hoechst, Federal Republic of Germany -----	54
Pigment Yellow 83 (C.I. 20,000), an aqueous dispersion of a yellow disazo pigment dye sold under the trade name Permanent Gelb HR Colanyl Teig by Farbwerke Hoechst AG, Frankfurt (M), Hoechst, Federal Republic of Germany -----	15
40% by weight aqueous dispersion of polyethylene having a particle size of less than 0.1 μ and an average molecular weight comprised between 15,000 and 30,000 -----	156
20% by weight aqueous solution of poly-N-vinylpyrrolidone (average molecular weight 30,000) -----	60
5% by weight aqueous solution of caseine -----	40
5% by weight aqueous solution of a wetting agent: ¹ -----	40
30% by weight aqueous dispersion of colloidal silica having an average particle size of 25 nm. -----	83
Ethanol -----	82

¹ Formula :



After drying at 50° C. the heat-sensitive layer was brought in contact with the infrared absorbing indicia of a printed text on paper and exposed to infrared radiation in an apparatus known as a "Thermographic Secretary Copying Machine" marketed by Minnesota Mining and Manufacturing Company, St. Paul, Minn., U.S.A. Due to the selective absorption of the infrared rays in the infrared absorbing indicia of the original, and the transfer of the heat produced therein into the thermosensitive recording layer, the latter obtained an image-wise decrease in water-permeability and could be selectively washed off

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in the unheated portions. The non-heated portions were washed off with a soft rotating roller of foamed rubber wetted with water at room temperature.

A positive coloured reproduction of the printed text legible through the transparent support and suited for over-heat projection was obtained.

EXAMPLE 11

To a subbed poly(ethylene terephthalate) support of 0.1 mm. thickness containing a semi-transparent coating as described in Example 9 a subbing layer for a thermosensitive layer was applied, the coating composition of the subbing layer being the following:

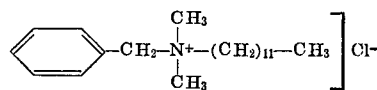
Water -----	756
40% by weight aqueous dispersion of polyethylene having a particle size of less than 0.1 μ and an average molecular weight comprised between 15,000 and 30,000 -----	40
35% by weight aqueous dispersion (latex) of a copolymer of butadiene, styrene, acrylonitrile and methacrylic acid (45:33:7:15% by weight) -----	4
30% aqueous dispersion of colloidal silica having an average particle size of 25 nm. -----	100
Ethanol -----	100

The coating proceeded at a ratio of 15 g. per sq. m.

The subbing layer thus obtained was coated with the composition of a thermosensitive layer in a ratio of 20 g. per sq. m.:

Water -----	432
Pigment Green 7 (C.I. 74,260), an aqueous dispersion of a polychlorinated copper phthalocyanine pigment dye sold under the trade name Heliogen-grün GV Colanyl Teig by Badische Anilin- & Soda-Fabrik A. G., Ludwigshafen/Rh., Federal Republic of Germany -----	110
40% by weight aqueous dispersion of polyethylene having a particle size of less than 0.1 μ and an average molecular weight comprised between 15,000 and 30,000 -----	156
20% by weight aqueous solution of poly-N-vinylpyrrolidone (average molecular weight 30,000) -----	80
5% by weight aqueous solution of a wetting agent: ¹ -----	40
30% aqueous dispersion of colloidal silica having an average particle size of 25 nm. -----	82
Ethanol -----	82

¹ Formula :



After drying at 50° C. the recording material was image-wise heated and developed as described in Example 10. A positive green image on a semi-transparent support was obtained.

We claim:

1. In a thermographic method of recording information by the steps of exposing a heat-sensitive recording material comprising a heat-sensitive water-permeable recording layer containing hydrophobic thermoplastic particles dispersed in a continuous phase of a hydrophilic binding agent soluble in an aqueous liquid to heat applied in a pattern according to said information, said heat being applied in an amount sufficient to coalesce said hydrophobic thermoplastic particles and thereby reduce the water-permeability of said layer in the heated areas thereof, and treating said exposed material with an aqueous liquid to remove the unheated areas of the recording layer, the improvement of increasing the resistance to removal of the heated portions of said record-

ing layer by providing in underlying contacting relation to said recording layer an underlayer which contains at least one thermoplastic substance having a hydrophobic character and a melting or softening point such that said substance remains adherent to the coalesced hydrophobic thermoplastic particles contained in the hydrophilic binder of the recording layer upon the information-wise heating of the heat-sensitive recording material, and wherein said interlayer is characterized by a lesser water-permeability and removability with water than said recording layer.

2. A method according to claim 1, wherein said interlayer comprises a dispersion of thermoplastic polymer particles in a continuous phase of hydrophilic binder.

3. A method according to claim 1, wherein said interlayer contains as the thermoplastic substance hydrophobic thermoplastic polymer particles in a hydrophilic binding agent that is less soluble in water than the hydrophilic binding agent of the recording layer.

4. A method according to claim 1, wherein said interlayer comprises a continuous phase of hydrophobic thermoplastic polymer containing hydrophilic pigment particles.

5. A method according to claim 4, wherein said interlayer includes a hydrophilic binding agent for said pigment particles.

6. A method according to claim 4, wherein said interlayer has been prepared from a latex the polymer particles of which coalesce on drying the coated layer at room temperature and which contains optionally hydrophilic pigment particles.

7. A method according to claim 1, wherein said interlayer consists essentially of coalesced hydrophobic thermoplastic polymer particles.

8. A method according to claim 2, wherein said interlayer contains a hydrophilic binding agent in an amount smaller than contained in the recording layer.

9. A method according to claim 1, wherein said interlayer contains a hydrophobic thermoplastic substance that has a chemical structure identical to that of the thermoplastic hydrophobic polymer particles contained in the recording layer.

10. A method according to claim 1, wherein said interlayer contains a hydrophobic thermoplastic substance that has a chemical structure different from the hydrophobic thermoplastic polymer particles contained in the recording layer but which wet or adhere to each other in fused or softened state.

11. A method according to claim 1, wherein said interlayer contains a hydrophobic thermoplastic substance that is compatible in fused state with the hydrophobic thermoplastic polymer particles of the recording layer.

12. A method according to claim 1, wherein the hydrophobic thermoplastic polymer particles of said recording layer stand in heat-conductive relationship with at least one substance, which converts absorbed electromagnetic radiation into heat energy, said recording layer is information-wise exposed to electromagnetic radiation the intensity and duration of which are such that in consequence of the absorption thereof by said substance a record is formed in terms of a different in water-solubility or swelling power in water of different portions of the recording layer, which recording layer after the exposure is treated with an aqueous liquid in order to remove the non-exposed portions of the recording layer.

13. A method according to claim 1, wherein the information is recorded by heat-transfer from the image markings of an original which is held in contact with the recording layer during the exposure of the original to electromagnetic radiation heating the image markings.

14. A method according to claim 1, wherein the proportion in the recording layer of said polymer particles relative to the hydrophilic binder, has a weight ratio of at least 1:1.

15. A method according to claim 2, wherein the hydrophobic polymer particles and hydrophilic binder are

present in the interlayer in a weight ratio of at least 1:1.

16. A method according to claim 1, wherein a hydrophilic binding agent is present in the recording layer which binding agent is soluble in water at room temperature.

17. A method according to claim 2, wherein said polymer particles range in size from 0.1μ to 50μ .

18. A method according to claim 2, wherein said polymer particles are latex polymer particles.

19. A method according to claim 2, wherein said particles are polyethylene particles.

20. A method according to claim 12, wherein a flashlamp is said radiation source.

21. A method according to claim 12, wherein said informationwise irradiation of the recording layer is applied for a period of less than 10^{-1} second.

22. A method according to claim 12, wherein said informationwise irradiation of the recording material is applied for a period of time between 10^{-2} and 10^{-5} second.

23. A method according to claim 12, wherein the intensity of the radiation incident upon the recording material is at least 0.1 watt. sec. per sq. cm.

24. A method according to claim 12, wherein the recording material is exposed to light through a sheet bearing a visible image.

25. A method according to claim 12, wherein the recording material is exposed to light through a sheet bearing a visible image.

26. A method according to claim 1, wherein the recording layer contains a dark coloured or black pigment uniformly distributed in said layer.

27. A method according to claim 1, wherein the recording layer contains a dark coloured or black pigment uniformly distributed in said layer in such an amount that the recording layer possesses an optical density of at least 1.

28. A method according to claim 25, wherein the recording layer contains a dark coloured or black pigment uniformly distributed in said layer in such an amount that the recording layer possesses an optical density comprised between 0.25 and 0.80.

29. A method according to claim 2, wherein the said polymer particles possess a melting or softening point equal to or lower than that of the polymer particles in the recording layer.

30. A method according to claim 1, wherein the recording layer after the information-wise heating is treated with an aqueous liquid or water, whereby the portions of the recording layer corresponding with the non-heat-exposed areas are washed away thus forming a relief image.

31. A method according to claim 1, wherein the non-heated portions of the recording layer are transferred onto a receiving material by pressing the recording layer previously wetted with an aqueous liquid against a receiving material and subsequently separating it therefrom.

32. A heat-sensitive recording material containing a heat-sensitive recording layer comprising hydrophobic thermoplastic particles dispersed in a hydrophilic binder and in underlying contacting relation to said recording layer an underlayer having a hydrophilicity and removability with water less than that of said recording layer and which contains at least one thermoplastic substance having a hydrophobic character and a melting or softening point such that said substance remains adherent after heating to the heat coalesced hydrophobic thermoplastic particles contained in the hydrophilic binder of the recording layer.

33. A heat-sensitive recording material according to claim 32, wherein said underlayer comprises particles of a hydrophobic thermoplastic polymer in admixture with hydrophilic material, said underlayer having a hydrophilicity less than that of said recording layer, and said polymer particles having a softening temperature not higher than that of the polymer particles of the recording layer and being adapted when molten to fuse compatibly with the polymer particles of the recording layer when molten.

34. A heat-sensitive recording material according to claim 33, wherein the interlayer comprises a dispersion of

thermoplastic polymer particles in a continuous phase of hydrophilic binder.

35. A heat-sensitive recording material according to claim 34, wherein the interlayer contains as thermoplastic substances hydrophobic thermoplastic polymer particles in a hydrophilic binding agent that is less soluble in water than the hydrophilic binding agent of the recording layer.

36. A heat-sensitive recording material according to claim 33, wherein the interlayer comprises a continuous phase of hydrophobic thermoplastic polymer containing hydrophilic pigment particles.

37. A heat-sensitivity recording material according to claim 33, wherein the interlayer has been prepared from a latex the polymer particles of which coalesce on drying the coated layer at room temperature and which contains optionally hydrophilic pigment particles.

38. A heat-sensitive recording material according to claim 33, wherein the interlayer consists essentially of coalesced hydrophobic polymer particles.

39. A heat-sensitive recording material according to claim 34, wherein the interlayer contains a hydrophilic binding agent in an amount smaller than contained in the recording layer.

40. A heat-sensitive recording material according to claim 33, wherein the interlayer contains a hydrophobic thermoplastic substance having a chemical structure which is identical to that of the thermoplastic hydrophobic polymer particles contained in the recording layer.

41. A heat-sensitive recording material according to claim 33, wherein the interlayer contains a hydrophobic thermoplastic substance having a chemical structure different from the hydrophobic thermoplastic polymer particles contained in the recording layer but which wet or adhere to each other in a fused or softened state.

42. A heat-sensitive recording material according to claim 33, wherein the interlayer contains a hydrophobic thermoplastic substance(s) that is compatible in fused state with the hydrophobic thermoplastic particles of the recording layer.

43. A heat-sensitive recording material according to claim 33, wherein the recording layer contains in heat-conductive relationship with said polymer particles at least one substance, which converts absorbed electromagnetic radiation into heat energy.

44. A heat-sensitive recording material according to claim 43, wherein said substance is carbon black.

45. A heat-sensitive recording material according to claim 33, wherein the recording layer contains coloured pigments or dyes.

46. A heat-sensitive recording material according to claim 33, wherein in the recording layer said polymer particles are present in the hydrophilic binder in a weight ratio of at least 1:1.

47. A heat-sensitive recording material according to claim 34, wherein the interlayer comprises the hydrophobic polymer particles and hydrophilic binder in a weight ratio of at least 1:1.

48. A heat-sensitive recording material according to claim 33, wherein the recording layer and the interlayer contain latex polymer particles.

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